Hybrid sensible/thermochemical storage of solar energy in cascades of redox-oxide-pair-based porous ceramics

Christos Agrafiotis, Andreas Becker, Lamark deOliveira,
Martin Roeb, Christian Sattler

Institute of Solar Research
DLR/ Deutsches Zentrum für Luft- und Raumfahrt/
German Aerospace Center
Linder Höhe, 51147 Köln, Germany

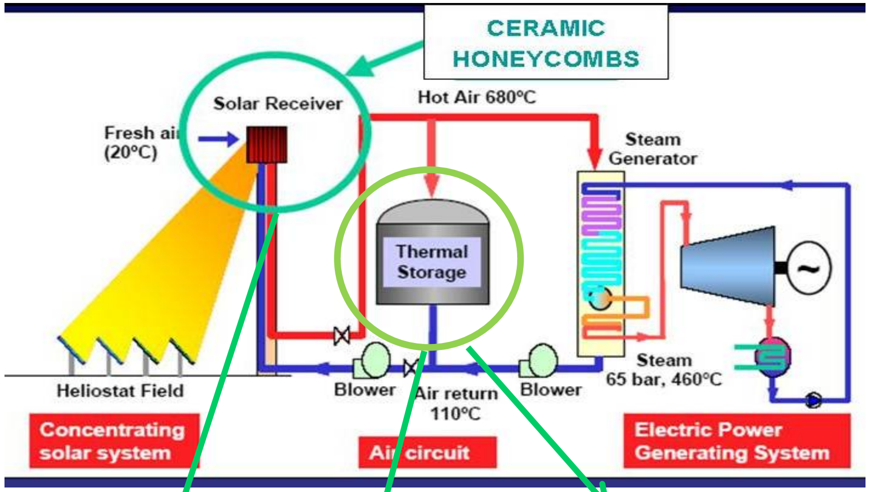
Outline:

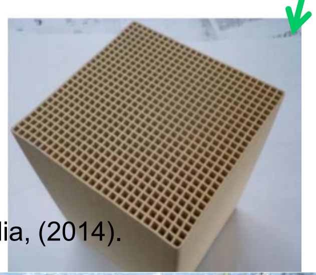
- Solar Energy Storage in air-operated Solar (Tower) Thermal Power Plants (STPPs)
- ThermoChemical Storage (TCS) principles and redox oxide pairs
- Some new ideas on redox-oxide-based porous ceramics for TCS in STPPs
- From laboratory to solar testing
- Conclusions, current and future work

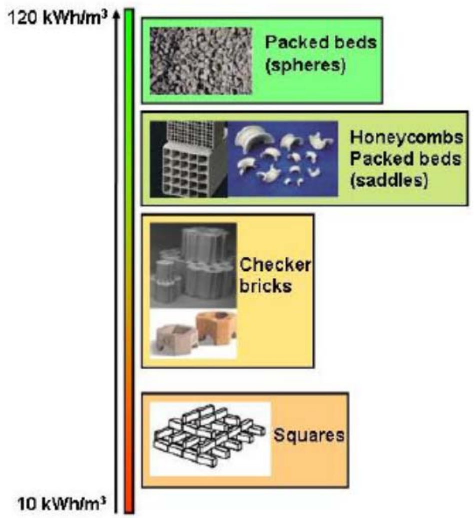
Air-operated CSP Plants (Solar Tower Jülich/STJ)

- HTF: Air at atmospheric pressure, heated up to about 700ºC and then powering a steam generator.

- Sensible heat storage : TES by temperature increase (cp ΔT)







Storage design specifications	
Inlet Temperature (Charge/ Discharge)	680 °C / 120 °C
Outlet temperature (Charge/Discharge)	680-640 °C 120-150 °C
Charge mass flow	9.4 kg/s
Discharge heat rate	5.7 MWth
Full load discharge period	1.5 h
Pressure loss	< 1500 Pa

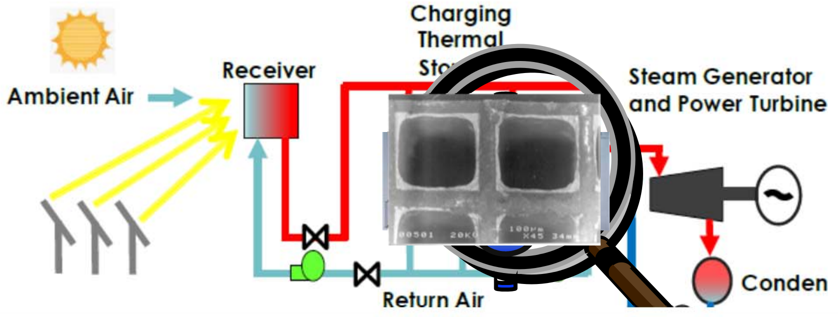
Table 2 Inventory

Honeycombs	60 x 60 cells
Brick dimensions	150 x 150 x 150 (mm)
Material	Alumina porcelain (C130)
Bulk density	2700 kg/m^3
Specific heat capacity	0.88 kJ/(kg K)
Thermal conductivity	2.1 W/(m K)
Heating surface	1180 m^2/m^3
Free cross section	69%

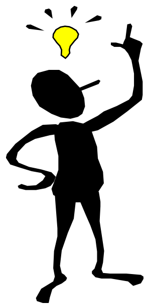
S. Zunft, et al.:SolarPACES, (2009); (2010); JSEE (2011); Energy Procedia, (2014).

From TES with sensible heat to hybrid sensible-thermochemical storage with redox oxides

On Sun

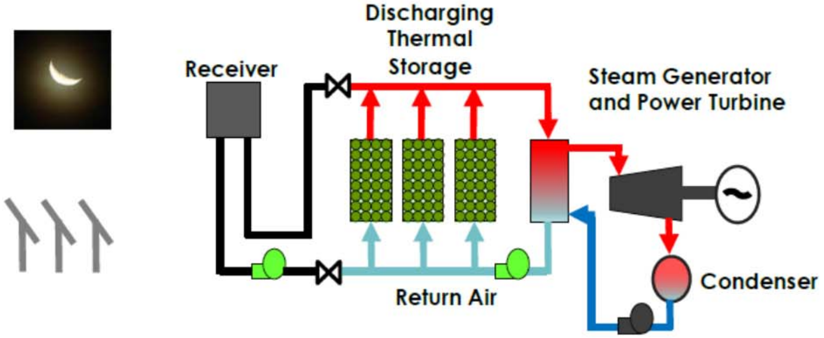


$MO_{2x+1} \rightarrow MO + xO_2$ ⟶ On sun endo. (charge)



Increase the volumetric storage density instead of the storage volume: “coat with/ make of” honeycombs with redox oxide

Off Sun



$MO + xO_2 \rightarrow MnO_{2x+1}$ ⟶ Off sun exo. (discharge)

Table 2.1
Metal Oxide Systems Applicable to TES Based on Thermodynamics Considerations

Reaction				Temperature (°C)	ΔH (kJ/mole oxide)	Storage Density (kJ/kg)
Cr_5O_{12}	→	$2.5Cr_2O_3$	$+ 2.25O_2$	110	126.0	279
$2Li_2O_2$	→	$2Li_2O$	$+ O_2$	150	68.2	1483
$2Mg_2O$	→	$2MgO$	$+ O_2$	205	21.8	505
$2PbO_2$	→	$2PbO$	$+ O_2$	405	62.8	262
$2PtO_2$	→	$2PtO$	$+ O_2$	420	62.8	277
$2Sb_2O_5$	→	$2Sb_2O_4$	$+ O_2$	515	92.5	286
$4MnO_2$	→	$2Mn_2O_3$	$+ O_2$	530	41.8	481
$6UO_3$	→	$6U_3O_8$	$+ O_2$	670	35.2	123
$2BaO_2$	→	$2BaO$	$+ O_2$	885	72.5	474
$2Co_3O_4$	→	$6CoO$	$+ O_2$	890	202.5	844
Rh_2O_3	→	Rh_2O	$+ O_2$	970	249.2	981
$6Mn_2O_3$	→	$4Mn_3O_4$	$+ O_2$	1000	31.9	202
$4CuO$	→	$2Cu_2O$	$+ O_2$	1120	64.5	811
$6Fe_2O_3$	→	$4Fe_3O_4$	$+ O_2$	1400	79.2	496
$2V_2O_5$	→	$2V_2O_4$	$+ O_2$	1560	180.7	993
$2Mn_3O_4$	→	$6MnO$	$+ O_2$	1700	194.6	850

General Atomics: GA–C27137: THERMOCHEMICAL HEAT STORAGE FOR CONCENTRATED SOLAR POWER THERMOCHEMICAL SYSTEM REACTOR DESIGN FOR THERMAL ENERGY STORAGE ; Phase II Final Report, 2011

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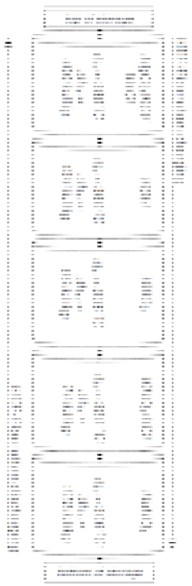
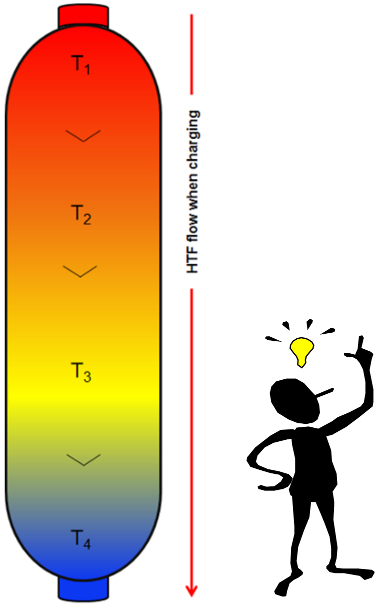
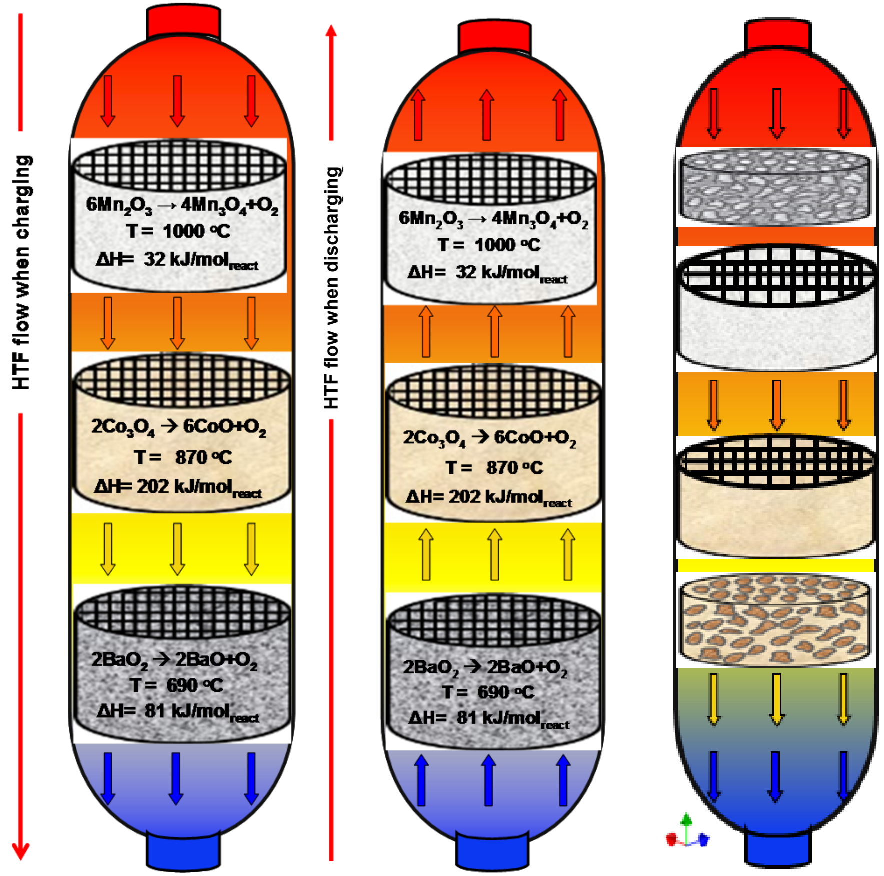
Cascaded ThermoChemical Storage (CTCS)

- A cascade of different redox oxide materials can be combined with various porous structures along as well “across” the reactor/heat exchanger.







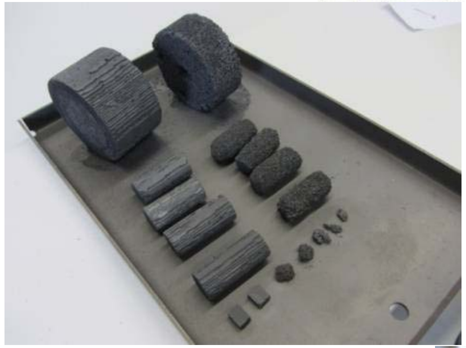
F. Dinter, M. Geyer, R. Tamme, Springer-Verlag, Berlin, (1991); Michels and Pitz-Paal, Solar Energy, 81 829–837, 2007.

TCS reactor/heat exchanger with spatial variation of functional materials and porosity in three dimensions, (C. Agrafiotis and R. Pitz-Paal, Patent Application Filed 2013).

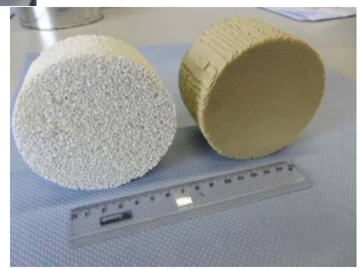
Tests Scale Evolution (single-oxide or cascaded testing)

TGA

Lab-scale furnace test rig



Solar receivers



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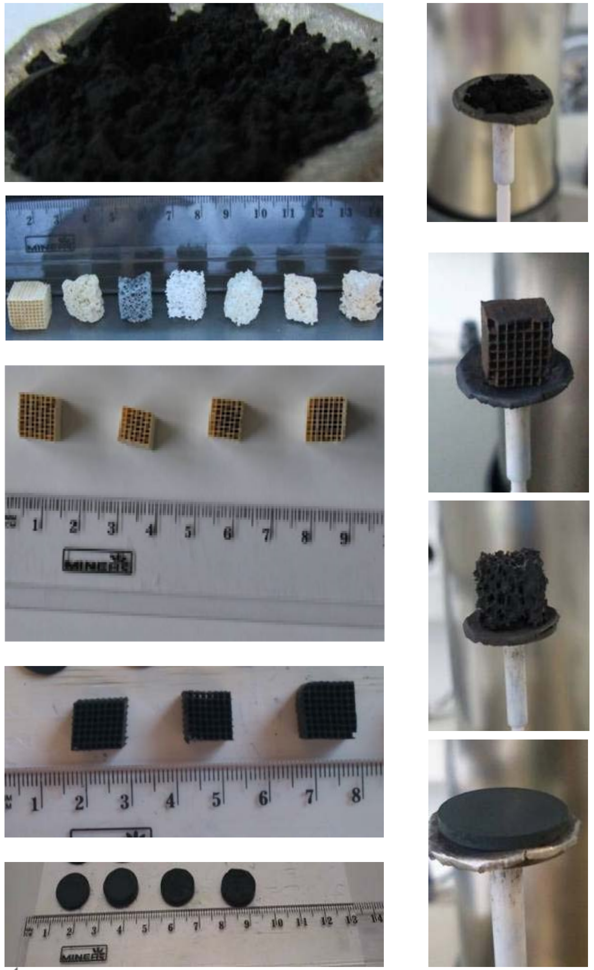
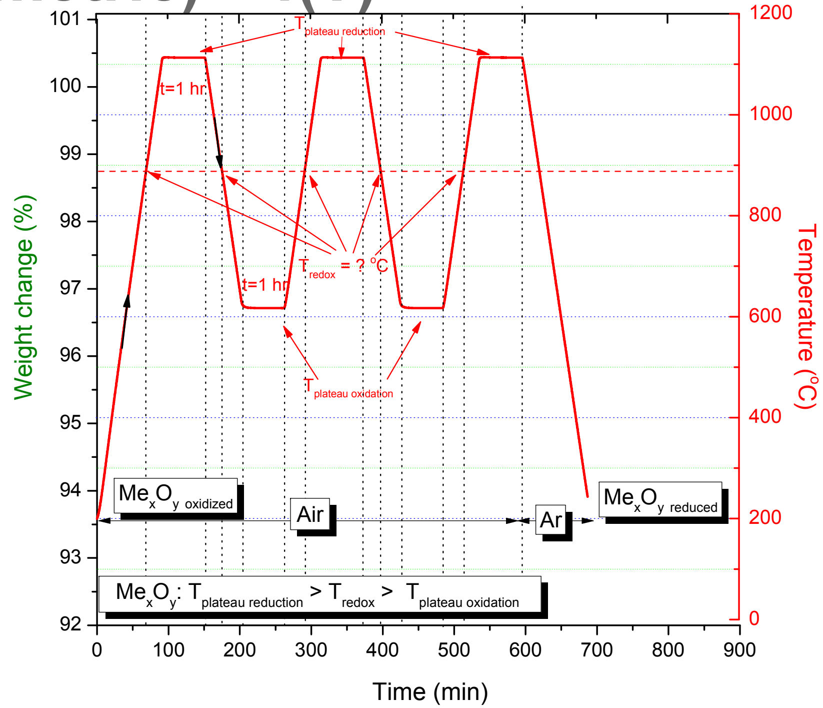
TGA (DSC) rig: Cyclic reduction – oxidation protocol weight change (vs. stoichiometric) = f(T)

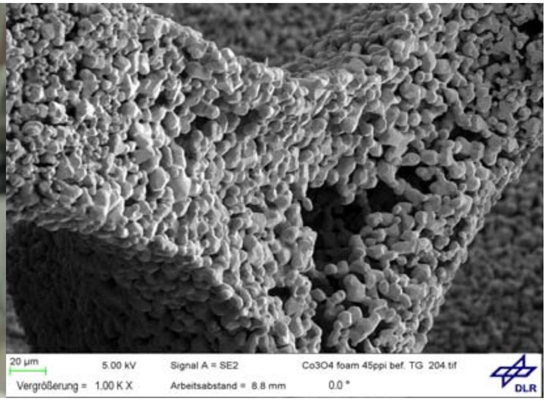


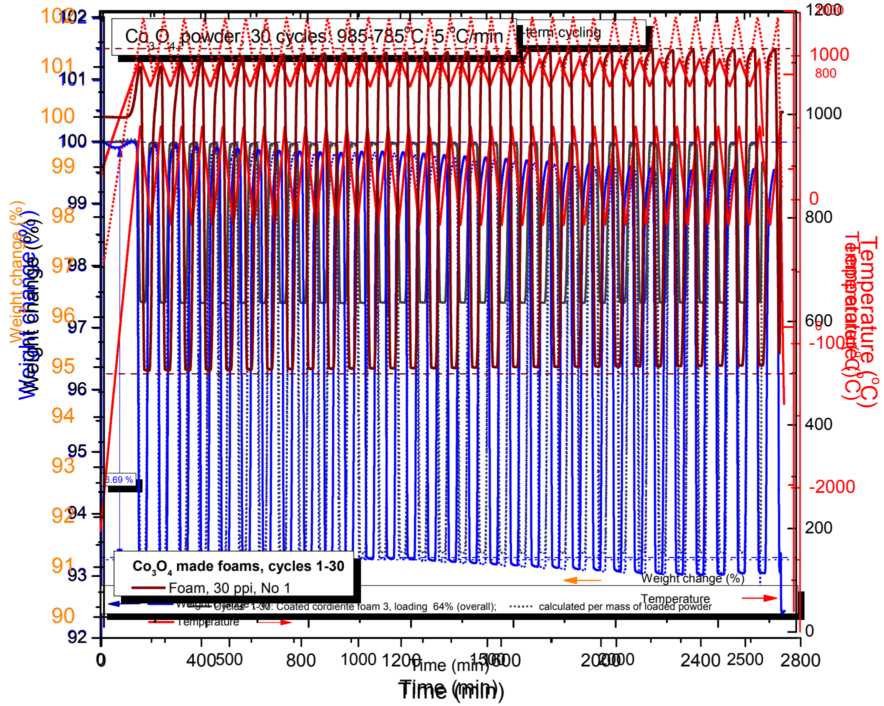


Reaction	T_{red} (°C)	Max. wt. loss (%)
$2\ BaO_2 + \Delta H \rightarrow 2\ BaO + O_2$	690	-9.45
$2\ Co_3O_4 + \Delta H \rightarrow 6\ CoO + O_2$	870	-6.64
$6\ Mn_2O_3 + \Delta H \rightarrow 4\ Mn_3O_4 + O_2$	950	-3.38
$4\ CuO + \Delta H \rightarrow 2\ Cu_2O + O_2$	1030	-10.01

TGA: Co_3O_4 /CoO

- Co_3O_4 can operate in a quantitative, cyclic and fully reversible reduction/ oxidation mode within 800-1000°C (950°C).
- As powder, coated on honeycombs/ foams or shaped in foams.

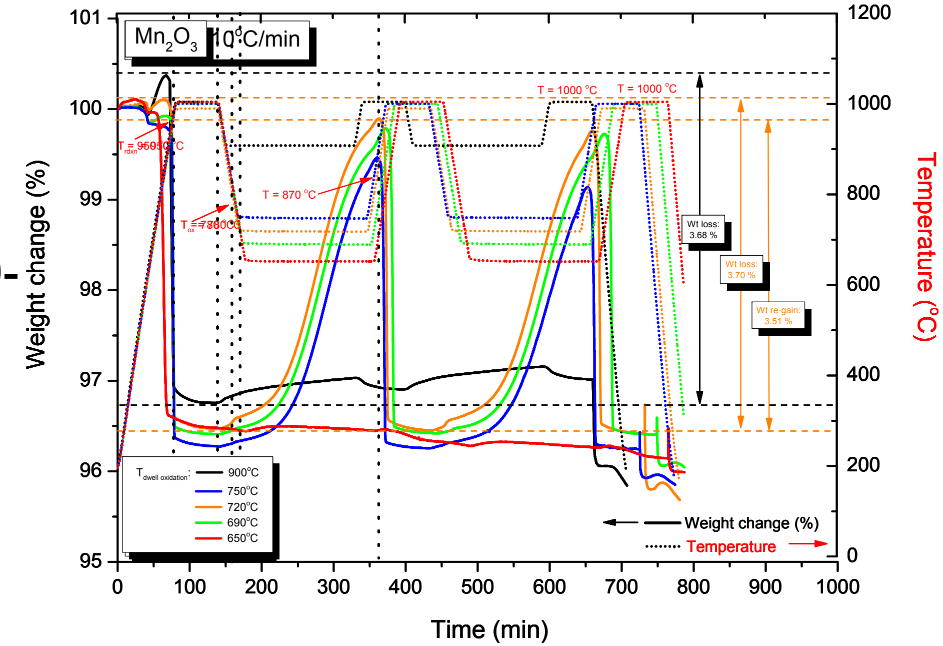


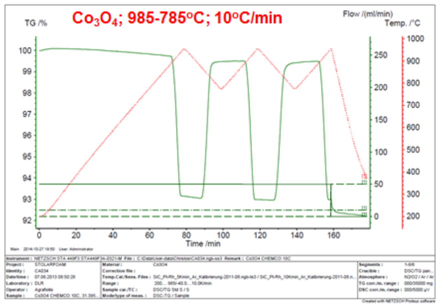


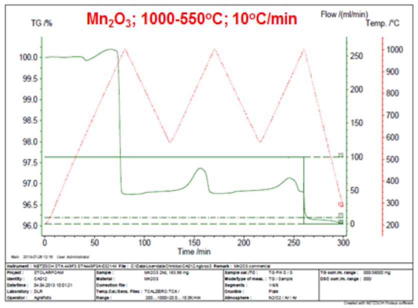
Agrafiotis, Roeb, Schmücker, Sattler, Solar Energy, Parts I, II, III (2014), (2015).

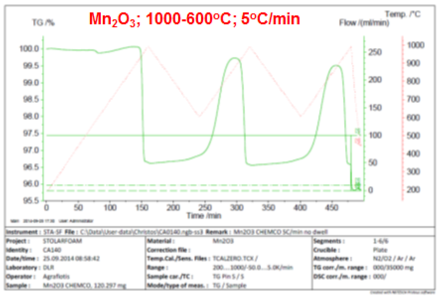
TGA: Mn_2O_3/Mn_3O_4

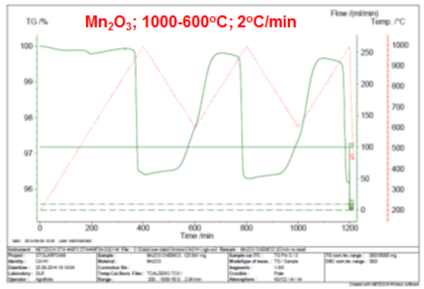
- Mn_2O_3: reduction fast, stoichiometric; but large temperature "gap" between reduction (≈950°C) - oxidation (≈780-690°C) !!
- Very narrow temperature range (≈690-750°C) within which Mn_2O_3 re-oxidation is significant.
- Mn_2O_3 re-oxidation is slow and needs extended dwell at the optimum temperature (range) for completion.
- Can be also achieved with slow rates and no dwell as shown below.











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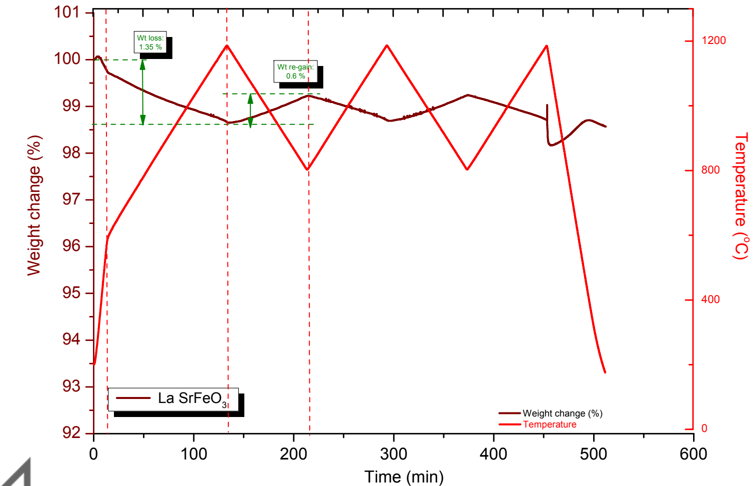
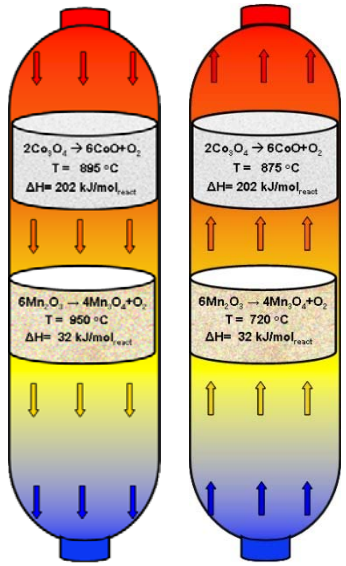
TGA: Other oxides

- CuO/Cu_2O: reduction temperature very close to m.p. of Cu_2O (shrinkage and sintering); could not work reproducibly even for few (5 cycles).
- BaO_2/BaO: BaO reacts with CO_2 present in air to $BaCO_3$
- Perovskites: loose/gain (little) weight continuously with T (perhaps plus in a cascade but ΔH also very low):

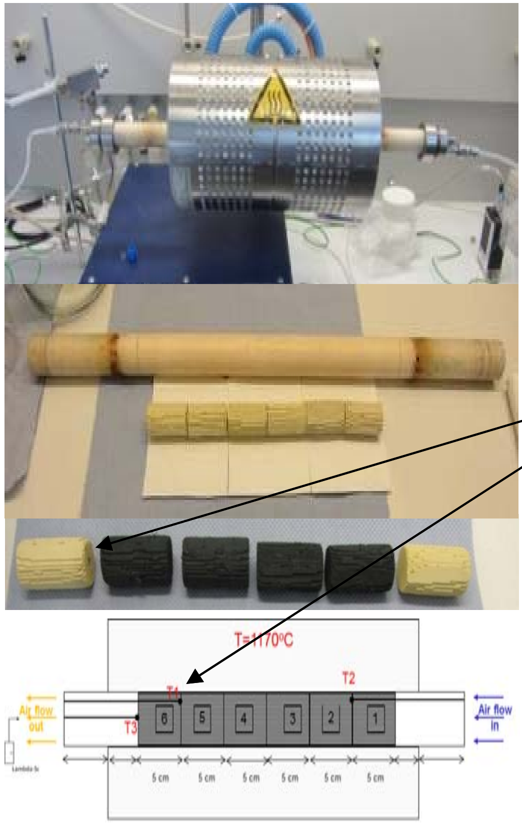


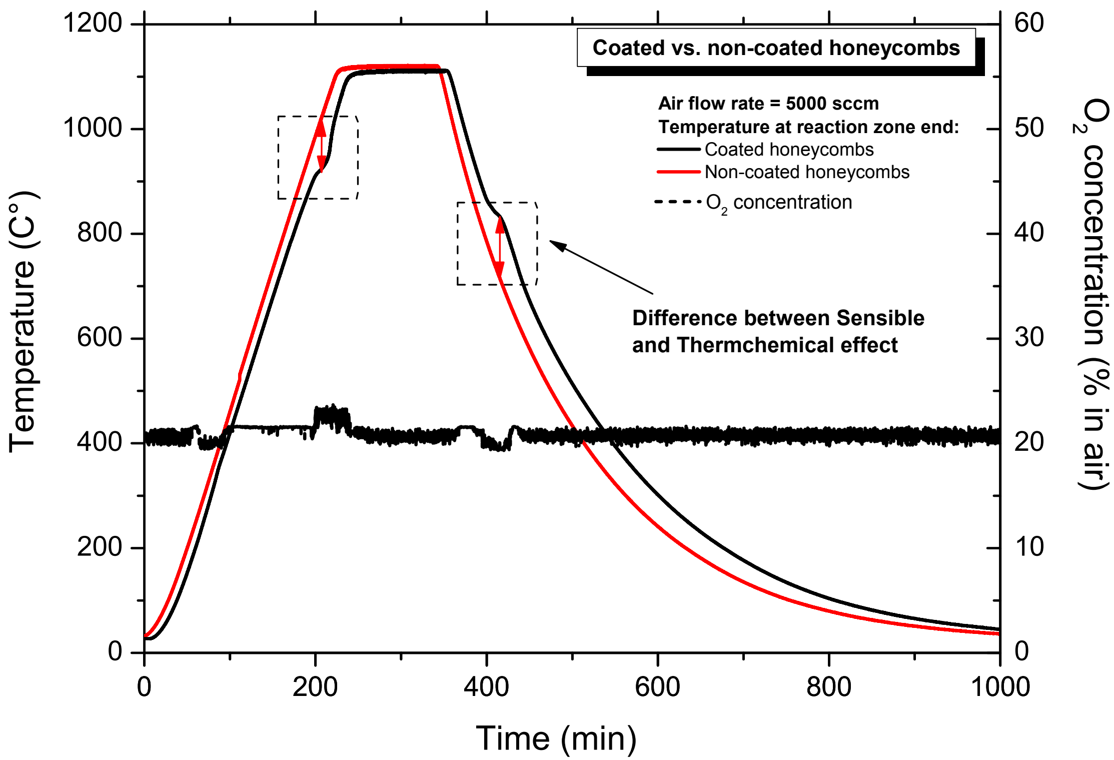
Reaction	ΔH (kJ/mol)	T_{red} (°C)	T_{ox} (°C)
$2\ Co_3O_4 + \Delta H \rightarrow 6\ CoO + O_2$	202.5	895	875
$6\ Mn_2O_3 + \Delta H \rightarrow 4\ Mn_3O_4 + O_2$	31.9	950	720



- Favourable Ts for oxidation but entire cascade needs T > 950°C during reduction

Furnace test rig: "Visualization" of Hybrid Sensible-TCS vs. Sensible-only storage effect





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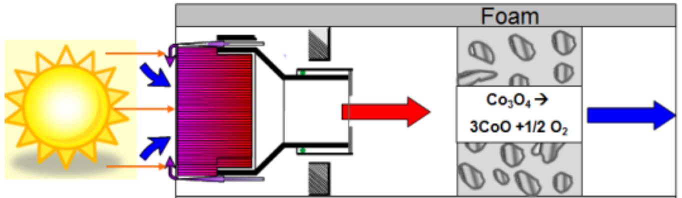
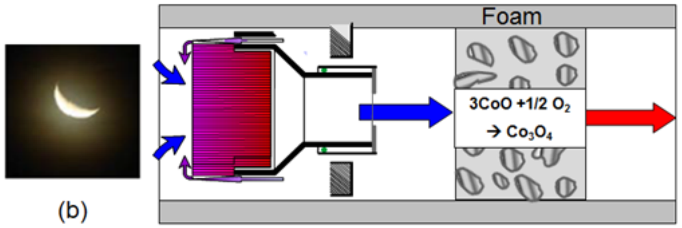
Solar furnace test rig: Receiver – storage modules assembly; 1st tests: T along non-coated storage module (sensible-only storage)



(a)



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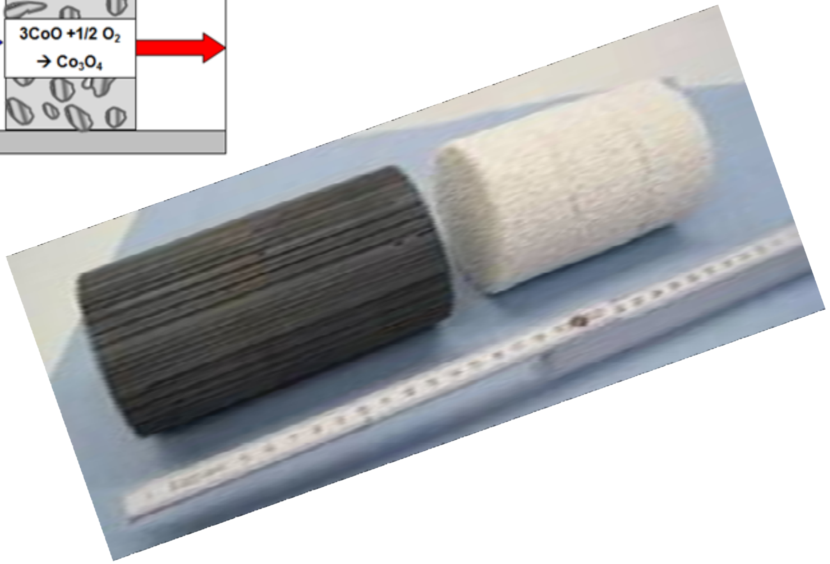
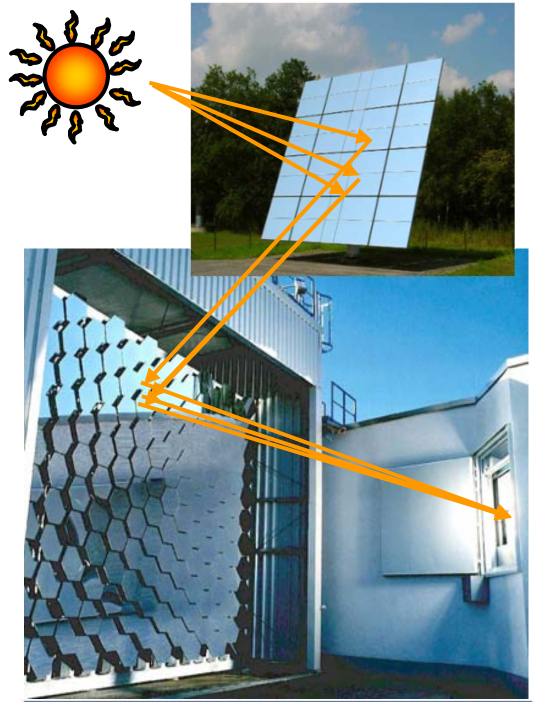
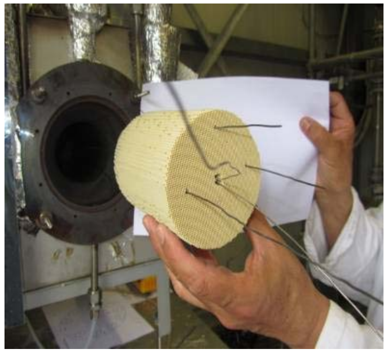




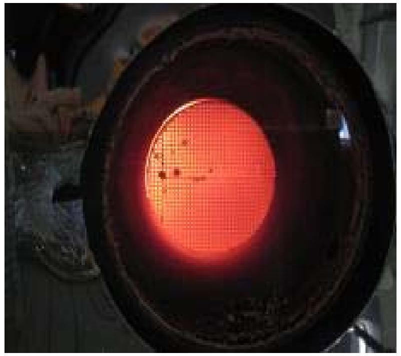
Comparative testing of storage module and (SiC) receiver types (190 slm)

3 Cordierite foams
30 ppi; L = 12 cm

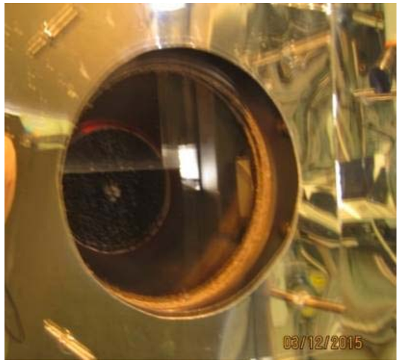
1 Cordierite honeycomb
400 cpsi L = 12 cm



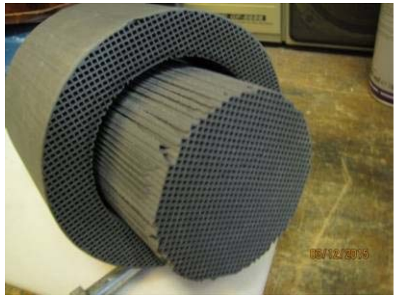
SiSiC honeycomb
90 cpsi; Schunk
Weight ≈1404 g
Length = 15 cm



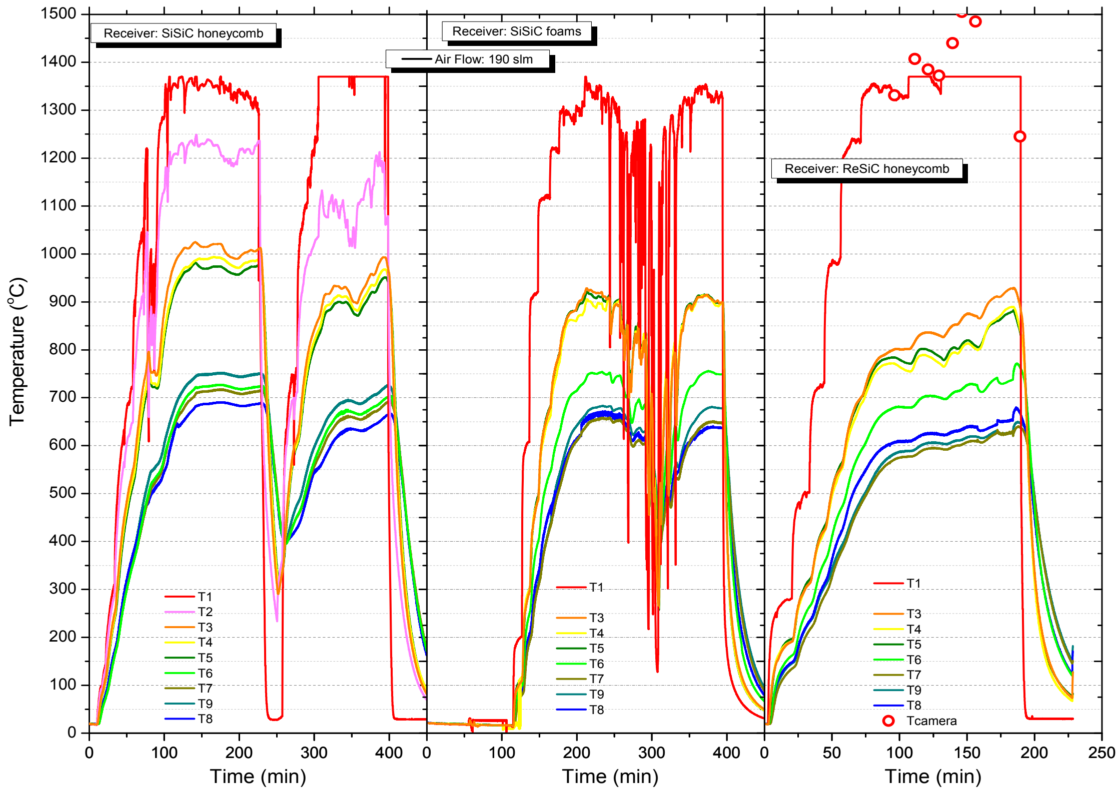
3 SiSiC foams
10 ppi; ERBICOL
Weight ≈ 246 g
Length = 12 cm

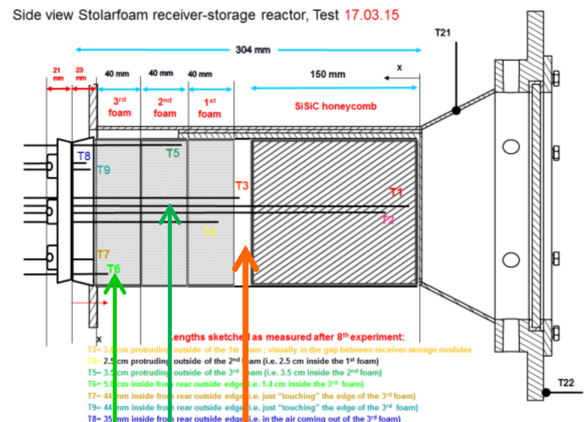


ReSiC honeycomb
90 cpsi; Stobbe TC
Weight ≈ 584 g
Length = 10 cm



Comparative performance of SiC receivers tested





T3≈1030°C T3≈930°C T3≈930°C

T5≈ 975°C T5≈915°C T5≈875°C

T6≈ 725°C T6≈755°C T6≈775°C

Conclusions:

- The construction modularity of the current state-of-the-art storage system in air-operated STPPs provides for implementation of concepts like **cascades of different redox oxide materials and spatial variation of solid material porosity in three dimensions,** to enhance utilization of heat transfer fluid and storage of its enthalpy.
- However: **limited variety of redox oxides available** within the particular temperature range. **Co_3O_4:** the most “reliable”, demonstrating full, quantitative cyclability within a narrow temperature range (“model system”).
- **Mn_2O_3: low cooling rates required for oxidation; large “temperature gap” between reduction/oxidation temperature.** This “disadvantage” though, can be rendered to benefit within a cascaded structure.
- Relatively high reduction temperatures of both Co_3O_4 ($T_{red} \approx 895^oC$) and Mn_2O_3 ($T_{red} \approx 950^oC$).
- Could be achieved in the solar furnace with currently available SiSiC honeycomb receivers: capability of solar-heating incoming air to ≈ 1050^oC, and two cordierite foams downstream (≈ 8 cm) to ≈ 950^oC demonstrated.

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- To **DLR** Programmdirektion Energie (PD-E) for funding through Project Thermochemical storage for CSP-applications based on Redox-Reactions – from materials to processes (REDOXSTORE).

Thank you for your attention !

- christos.agrafiotis@dlr.de
- martin.roeb@dlr.de
- christian.sattler@dlr.de